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Block copolymer-directed metal nanoparticle morphogenesis and organization

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ABSTRACT

Advances in the nanoscale design of polymeric, "soft" materials and of metallic, "hard" materials can converge at the "interfaces" to form hybrid nanomaterials with interesting features. Novel optical, magnetic, electronic, and catalytic properties are conferred by metal nanoparticles, depending on their morphology (size and shape), surface properties, and long-range organization. We review here the utilization of block copolymers for the controlled synthesis and stabilization of metal nanoparticles. Solvated block copolymers can provide nanoscale environments of varying and tunable shape, dimensions, mobility, local polarity, concentration, and reactivity. In particular, block copolymers containing poly(ethylene oxide) can exhibit multiple functions on the basis of their organization at the intra-polymer level (i.e., crown ether-like cavities that bind and reduce metal ions), and at the supramolecular level (surface-adsorbed micelles, and ordered arrays of micelles). These block copolymers can thus initiate metal nanoparticle formation, and control the nanoparticle size and shape. The physically adsorbed block copolymers, which can be subsequently removed or exchanged with other functional ligands, stabilize the nanoparticles and can facilitate their integration into diverse processes and products. Block copolymers can be further useful in promoting long-range nanoparticle organization. Several studies have elucidated the nanoparticle synthesis and stabilization mechanism, optimized the conditions for different outcomes, extended the ranges of materials obtained and applications impacted, and generalized the scope of this functional polymer-based nanoparticle synthesis methodology.

1. Introduction

Advances in the nanoscale design of "soft" materials (such as block copolymers) and of "hard" materials (e.g., metal or semiconductor nanocrystals) can converge at the "interfaces". Hybrid nanomaterials with novel properties can result from the organization (locally and over longer range) of polymer assemblies and nanoparticles.

Block copolymers, at sufficiently strong degrees of block segregation, self-organize into nanoscale domains with an interfacial curvature and corresponding domain structure that depend on the volume fraction of one block relative to that of the other block [1–5]. Both the degree of block segregation and the block volume fraction can be modulated by the addition of selective solvents, resulting in increasing diversity of structure, range of conditions where a certain structure is stable, domain sizes, and domain accessibility, in faster molecular diffusivity and structural response times, but also in reduced temperature and mechanical stability [6–8].

Nanoparticles are notable for their size-dependent optical, magnetic, electronic, and catalytic properties [9–13]. Metal nanoparticles, in particular gold, are being considered in wide-ranging applications such as photonics, information storage, electronic and optical detection systems, therapeutics, diagnostics, photovoltaics, and

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catalysis [9–19]. While the chemical composition of a nanoparticle is important, even more important are the size and shape of the nanoparticle and its surface/colloidal properties. Different nanoparticle morphologies can result from altering the relative growth rates of different crystallographic facets by the selective localization of surface-modifying or capping agents, but also by the modulation of nucleation and reaction parameters such as time, temperature, and reagent type and concentration [20].

The development of simple and versatile methods for the preparation of nanoparticles in a size- and shape-controlled manner has attracted significant attention in the literature [21,22]. Polymers have proven very useful to this end. Reagents can be loaded into and react with functional polymers. The nanoscale domains formed by block copolymers can provide loci for the growth of nanoparticles [23–25], while the block architecture can facilitate both the modification of the nanoparticle surface and the long-range positioning of nanoparticles [26–30].

To realize the full potential of functional polymers for nanoparticle synthesis, a better insight into the relationship between polymer characteristics and particle formation is required. Such fundamental information will enable rational design of polymers to meet specific needs. Following the initial reports on the promise of certain block copolymers for the spontaneous synthesis of gold and silver nanoparticles, several research groups have pursued "green", water-based synthetic routes for the synthesis of metallic nanomaterials with the use of functional polymers as both reductants of the metal salt and capping agents of the resulting nanocrystals. Here we review literature that discusses the synthesis, morphology control, colloidal stabilization, and long-range organization of metal nanoparticles in functional polymer media. The review concludes with a discussion of possible applications and future prospects in this area.

2. Synthesis and stabilization of metal nanoparticles in aqueous poly(ethylene oxide)–poly(propylene oxide) block copolymer solutions

Metal nanoparticles are commonly produced by the reduction of metal ions in the presence of organic solvents and ligands. For example, the popular gold nanoparticle synthesis method developed by Brust et al. [31] involves the transfer of $AuCl_4^-$ in toluene or chloroform using tetraalkylammonium bromide, and its reduction in the organic solvent with sodium borohydride in the presence of alkylthiols. The nanoparticles thus synthesized are covered with strongly bound ligands that render them difficult to disperse in water, and may hinder further surface modification and functionalization. Compared to such a synthesis method, a methodology based on the use of an aqueous solvent and non-toxic chemicals should provide an environmentally benign route to the production of metal nanoparticles [32,33], and result in a product that can be easily integrated in applications that involve an aqueous milieu.

In aqueous solutions [34–37], gold nanoparticles have been typically produced from the chemical reduction of gold ions by reducing agents such as $NaBH_4$, citric acid, or ascorbic acid. Such reduction takes place with the aid of externally supplied energy such as photoirradiation [34], ultrasound irradiation [35], or heating [36] in the presence of one or more water-soluble polymers, surfactants or capping agents. Adequate control of the size and concentration of the dispersed particles can be achieved [34–37], and the surface-modifying or capping agents prevent nanoparticle aggregation [17]. While the most common strategy to achieve colloidal stability proceeds via the chemical binding of ligands to the surface of the nanoparticles, a covalent linkage between the ligand and the nanoparticle may alter the properties of the nanoparticles through a modification of their electronic density and the dielectric constant of the surrounding medium [38]. A strategy based on the physical adsorption of ligands such as block copolymers on the surface of the nanoparticles can preserve the intended properties of the nanomaterial [39]. Despite the progress achieved, concerns and problems with the preparation of metal nanoparticles remain, such as the byproducts from the reducing agent, the multiple synthesis and purification steps often required, and the high concentration of protective agents.

2.1. Spontaneous gold nanoparticle formation in PEO–PPO block copolymer solutions: mechanism

Many of the challenges and opportunities outlined above have attracted the attention of many researchers in recent years, including our group. In particular, we have discovered that poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymers can act as very efficient reductants and stabilizers in the single-step synthesis and stabilization of gold nanoparticles from hydrogen tetrachloroaureate hydrate ($HAuCl_4{\cdot}3H_2O$) in air-saturated aqueous solutions, at ambient temperature, and in the absence of any additional reductants or energy input [40,41]. This synthesis proceeds fast to completion (in less than 2 h), and is environmentally benign and economical since it involves only water and non-toxic, commercially available polymers (known as Pluronics or Poloxamers; refer to Table 1). The colloidal gold dispersions can remain highly stable for several years. Further, the same starting materials can lead to a variety of nanoparticle morphologies (e.g., spheres, plates, prisms, icosahedra) depending on the polymer PEO–PPO composition, molecular mass, and concentration. Compared to other methods for gold nanoparticle synthesis [9,17,21], this functional polymer-based methodology offers the advantages of ambient conditions, fast completion, minimal number of reactants, low cost, and a "ready-to-use" product. The later feature is particularly advantageous in biomedical applications of the gold nanostructures.

On the basis of systematic studies on the PEO–PPO–PEO block copolymer concentration dependence of the absorption spectra and the particle size, and on the $HAuCl_4$ reduction kinetics [42], it was proposed that gold nanoparticles formation in the aqueous functional polymer solutions comprises three main steps: (1) initial reduction of metal ions in crown-ether-like domains formed by the PEO-containing block copolymer in solution, (2) absorption of block

Table 1
Properties of various poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymers (commercially available by BASF as Pluronics).

Pluronic	Molecular mass	PEO (wt.%)	PPO block mol. mass	PEO block mol. mass	cmc (mM) (25 °C)	Nominal formula
L43	1850	30	1295	555		$EO_6PO_{22}EO_6$
L44	2200	40	1320	880		$EO_{10}PO_{23}EO_{10}$
L62	2500	20	2000	500		$EO_6PO_{34}EO_6$
L64	2900	40	1740	1160	26	$EO_{13}PO_{30}EO_{13}$
P65	3400	50	1700	1700	38	$EO_{19}PO_{29}EO_{19}$
F68	8400	80	1680	6720	320	$EO_{76}PO_{29}EO_{76}$
P84	4200	40	2520	1680	6.2	$EO_{19}PO_{43}EO_{19}$
P85	4600	50	2300	2300	8.7	$EO_{26}PO_{40}EO_{26}$
F88	11,400	80	2280	9120	11	$EO_{103}PO_{39}EO_{103}$
P103	4950	30	3465	1485	0.14	$EO_{17}PO_{60}EO_{17}$
P104	5900	40	3540	2360	0.51	$EO_{27}PO_{61}EO_{27}$
P105	6500	50	3250	3250	0.46	$EO_{37}PO_{56}EO_{37}$
F108	14,600	80	2920	11,680	3.1	$EO_{132}PO_{50}EO_{132}$
P123	5750	30	4025	1725	0.05	$EO_{19}PO_{69}EO_{19}$
F127	12,600	70	3780	8820	0.55	$EO_{100}PO_{65}EO_{100}$

copolymer on the gold clusters initially formed, and localized reduction of metal ions on the surface of these gold clusters to increase their size, and (3) growth of metal particles to a certain size and shape that are dictated by the block copolymers that stabilize them [42]. While both PEO and PPO blocks contribute to the gold ion reduction (step 1), the PEO contribution appears to be dominant. In step 2, the adsorption of block copolymers on the surface of gold clusters takes place because of the amphiphilic character of the block copolymer (that emanates from the hydrophobicity of PPO). The size of the gold nanoparticles produced tends to increase with increasing reaction activity caused by the block copolymer molecular mass, but can be limited by the adsorption of the block copolymers due to their amphiphilic character. The proposed mechanism is supported by various data, as discussed below.

2.2. Reduction of $HAuCl_4$ to form gold nanoparticles: the roles of PEO and hydrophobic block

The aforementioned reaction mechanism suggests that an increase in the PEO chain length (molecular mass) favors the reduction of $HAuCl_4$ and the formation of particles. Indeed, the absorbance changes indicative of $HAuCl_4$ reduction and nanoparticle formation, as well as the average nanoparticle size, were found to follow the order of increasing PEO block length (Pluronic P103 < P105 < F127 < F108), which is consistent with an increase in reaction activity [42]. PEO can form cavities (pseudo-crown ethers) that bind metal ions [43]. Reduction of bound $AuCl_4^-$ ions proceeds via oxidation of the oxyethylene and oxypropylene segments by the metal center. The cyclization of the PEO chain is induced by ion–dipole interactions between the templating ion and the electron lone pairs of the oxyethylene linkages [44]. Several oxygen atoms in the PEO chain interact with one metal ion, and therefore the strength of the attraction depends on the length of the PEO chain. Thus we believe this mechanism to be primarily responsible for metal ion reduction by PEO-containing polymers [42].

Valuable insights on the initial stages of gold nanoparticle formation by the reduction of $HAuCl_4$ in aqueous PEO–PPO–PEO block copolymer solutions have emerged from a recent time resolved study that utilized X-ray absorption spectroscopy (XAS) to probe in situ the reduction of gold from Au(III) to Au(0), and small-angle X-ray scattering (SAXS) to record the size distribution of the formed nanoparticles [45]. According to this study, the reduction of Au(III) to Au(0) commenced immediately upon mixing the $HAuCl_4$ solution with the block copolymer (in this case, Pluronic F127) solution. The nanoparticles form in a "burst" process, whereby the final particle number is reached quickly. Subsequently, only the particle size increases over time. For the first few minutes of the reaction, the quantity of Au(0) was found higher than the quantity of gold located in the nanoparticles. This was attributed to the pseudo-crown ether effect of the PEO–PPO–PEO block copolymers, which kinetically stabilize gold atoms within their cavity [45]. Time-dependent UV spectra provided further evidence that the very first step of the synthesis was the formation of primary gold clusters composed of a few gold atoms [46].

In an effort to decouple the relative contributions of the PEO and the hydrophobic PPO block on the reduction of gold ions and the formation of gold nanoparticles, the absorbances at 240 nm (a measure of $AuCl_4^-$ concentration) and at 540 nm (a measure of nanoparticle concentration) were considered for many PEO–PPO–PEO block copolymers [42]. For block copolymers having shorter PEO block lengths, the absorbance at 240 nm decreased linearly, and that at 540 nm increased, with increasing block copolymer PPO length, indicating that PPO also plays a role in the reduction of gold ions and nanoparticle formation [42]. It appears that the particle size results from a competition between (i) a reaction activity enhancement by block copolymer concentration or PEO block length, and (ii) a decreased reactivity due to tight block copolymer adsorption on the gold nanoparticle surface favored by the hydrophobicity of the PPO blocks [42]. A comparison of PEO–PPO block copolymers to PEO–poly(styrene oxide) (PSO) block copolymers offered further information the role of the

hydrophobic block [47]. The time needed to complete the metal salt reduction was much longer in the case of the PEO–PSO block copolymers. This has been attributed to the greater hydrophobicity and tight packing of PEO–PSO block copolymers in aqueous solution, that disfavor the contact with $AuCl_4^{--}$ ions and their subsequent reduction [47]. The hydrophobic PSO block also affected steps 2 and 3 of the synthesis mechanism, by means of the preferential adsorption of the block copolymer on certain crystallographic planes (see related discussion in Section 4).

2.3. Role of solvent quality on nanoparticle synthesis

The complexation of metal ions with block copolymers in solution (related to step 1 of the synthesis mechanism) and on the nanoparticle surface (related to step 2) could be modulated by the quality of the solvent, since several properties of PEO–PPO–PEO block copolymers are strongly affected by it [48–55]. For example, the solvent quality of water becomes worse with increasing temperature, leading to lower critical micelle concentration (cmc) [48], higher surface adsorption [49], and micelles with denser PEO corona [51], while it becomes better when replacing water with formamide [50] or ethanol [51]. These features can provide opportunities to control the reactivity and resulting particle size. Two main factors were identified as important for controlling the competition between gold ion reduction in the bulk solution to form gold clusters (seeds) and on the surface of gold particles, and for the particle size determination: (i) block copolymer conformation or structure (e.g., loops vs. entanglements, non-associated polymers vs. micelles), and (ii) interactions between $AuCl_4^{--}$ ions and block copolymers (attractive ion–dipole interactions vs. repulsive interactions due to hydrophobicity) [56].

More specifically, a particle size increase with increased temperature was observed in aqueous solutions, that has been attributed to a combination of (a) a decrease in the number of gold seeds (reaction sites) due to a decrease in the number of non-associated polymers in solution and an increase in repulsive interactions between the $AuCl_4^-$ ions and the more hydrophobic PEO–PPO–PEO block copolymers, and (b) an enhanced gold ion reduction on the surface of seeds where the block copolymer predominantly resided due to their increased hydrophobicity [56]. The solvent quality of water can also become worse with increasing electrolyte concentration [57]. The addition of 0.7 M NaF to water enhanced the PEO–PPO–PEO block copolymer micelle hydrophobicity, significantly increased the stabilization capacity of the micelles, and favored spherical gold particles [46]. The importance of well-defined micelles with relatively dehydrated PEO corona for the reduction to occur has been further discussed more recently [58]. In formamide solutions, a lower reactivity and a higher particle size were observed compared to water, which were attributed to the shielding by formamide of ion–dipole interaction between $AuCl_4^-$ ions and block copolymers, shielding that overcomes the beneficial effects of formamide on the block copolymer conformation (lower micelle concentration) [56].

2.4. Silver nanoparticle formation in PEO–PPO block copolymer solutions

The solvent quality has been tailored to direct the reactivity of PEO–PPO block copolymers toward the synthesis of silver nanoparticles. PEO–PPO block copolymers dissolved in formamide at 100 °C can reduce silver nitrate ($AgNO_3$) to form Ag colloids with various morphologies (e.g., spherical nanoparticles, plates, wires) [59]. The morphology of Ag colloids was affected by the block copolymer PEO/PPO composition and sequence. For example, the more interfacially active Pluronic 25R4 PPO–PEO–PPO block copolymer ($PO_{19}EO_{33}PO_{19}$) produced spherical Ag nanoparticles, while the Pluronic P105 PEO–PPO–PEO block copolymer favored Ag nanowires. These morphologies are most likely determined in terms of a competition between (i) metal ion reduction activity in the bulk solution and on the surface of particles and/or among particle aggregates, and (ii) the colloidal stabilization modulated by the amphiphilic character of the block copolymers [59].

PEO–PPO–PEO block copolymers have been found useful as stabilizers in the synthesis of silver nanoparticles by the chemical reduction of $AgNO_3$ with excess of sodium borohydride, $NaBH_4$ [60]. Besides the stabilizing character, Pluronic L64 affected the kinetics of particle growth, and the size and optical properties of as-synthesized Ag nanoparticles [60]. Pluronic L64 had been previously used at a capping agent in the seeded growth synthesis of platinum nanoparticles (3.5–6.6 nm) by the reduction of H_2PtCl_6 in water with $NaBH_4$ [61].

2.5. Efficient stabilization of metal nanoparticles in aqueous PEO–PPO block copolymer solutions

The same PEO–PPO block copolymers that are responsible for the synthesis of the metal nanoparticles, also serve an important function as colloidal stabilizers for the nanoparticle dispersions. In an attempt to uncouple the nanoparticle formation and stabilization processes that take place in tandem, the stabilization function of PEO–PPO–PEO block copolymers was examined in aqueous dispersions of well-defined gold nanoparticles (~12 nm diameter) that had been previously synthesized through a citrate reduction procedure [39]. The stabilization of the gold nanoparticles was found to occur below the cmc of the PEO–PPO–PEO block copolymers. The nanoparticle colloidal stability increased with the polymer concentration, PEO and PPO block lengths, or the overall polymer length, with the length of the hydrophobic PPO block emerging as most important parameter. Among the various PEO–PPO–PEO block copolymers considered (Pluronics P123, P104, P84, F88, L62, L64, F108, P85, and P65; see Table 1), Pluronic F127 was found the most efficient toward colloidal stabilization [39]. The same group [62] considered also PEO–PPO diblock copolymers as stabilizers. The diblocks provided long-term colloidal stability above their cmc, whereas triblock copolymers can serve as stabilizers also below the cmc [62]. It was pointed out that the exceptional colloidal stability conferred by the PEO–PPO block copolymers, which interact non-covalently with the

gold nanoparticles, should be readily translated to other types of nanoparticles and/or amphiphilic polymers.

In a subsequent study, the structure of preformed gold particles that had been stabilized by PEO–PPO–PEO block copolymers was characterized using a range of techniques: transmission electron microscopy (TEM), dynamic light scattering, and small-angle neutron scattering (SANS) with contrast variation that matched the scattering length density of gold [63]. Gold nanoparticles were found individually embedded within globules of polymer, consistent with the colloidal stability of these systems, even under conditions for which block copolymer micelles would not form in solution. A core–shell morphology, with gold particles surrounded by a polymer shell, is demonstrated in Fig. 1 [63]. Gold was embedded in polymer in most cases, however, a few nanoparticles were not surrounded by polymer, and several polymer globules were not associated with nanoparticles. The same features were observed by cryo-TEM at conditions where the polymers remained in a hydrated state [63].

In a modeling study that nicely complements the aforementioned experiments, the formation and stabilization of gold nanoparticles in PEO–PPO–PEO block copolymer micelles was simulated with dissipative particle dynamics (DPD) [64]. The primary gold clusters that were experimentally observed in the early stage of gold nanoparticle formation were modeled as gold beads. These gold beads were shown to be aggregated into spherical particles, and to form stable polymer-gold colloids with the hydrophobic PO segments adsorbed on the surface of gold particles, and the hydrophilic EO segments exposed to water [64]. Increasing the polymer concentration, molecular mass, and PPO block length led to the formation of more uniform and more stable gold nanoparticles, in agreement with the picture emerging from experiments [64].

3. Spontaneous synthesis of metal nanoparticles in functional polymer solutions

The principle of having a single functional polymer that can serve in tandem as a reductant, morphogenic agent, and colloidal stabilizer for metal nanoparticles, as exemplified by the PEO–PPO block copolymers discussed above, can be readily extended to other polymers. In this section we highlight cases of spontaneous gold nanoparticle formation in solutions of polymers containing PEO and/or amines. These functional polymers can be linear, branched, or dendrimers, produced by simple or sophisticated chemistry, or even by nature (polypeptides). We note that recent literature has discussed the ability of certain ionic liquid solvents to act as reductants for metal nanoparticle synthesis [65–68], but we do not review this topic here.

3.1. PEO–PPO block copolymers with added amine functionality

Tetronics, which consist of four PEO–PPO arms linked at the center with a tertiary amine group, have been shown to act as both reductants and stabilizers in the one-pot aqueous solution synthesis of gold nanoparticles [69], with a synthesis mechanism analogous to that in PEO–PPO–PEO block copolymers. Low polymer/$AuCl_4^-$ molar ratios led

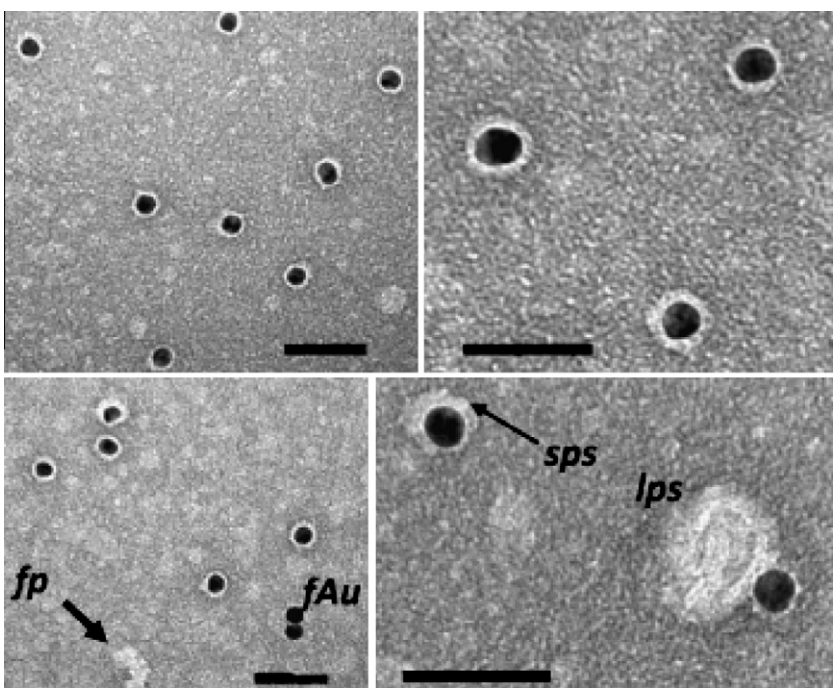

Fig. 1. TEM images of preformed gold nanoparticles coated with Pluronic F127 (concentration of 0.04 mM L^{-1}, ten times lower than the cmc). The gold particle core appears as dark contrast, due to negative staining with uranyl acetate, while the polymer has lighter contrast. The notations *sps*, *lps*, *fAu*, and *fp* indicate small polymer shell, large polymer shell, free gold particle, and free polymer nodule, respectively [63]. The scale bars are 50 nm.

to a low reduction rate that favored the formation of triangular or hexagonal nanoplates. At higher polymer/$AuCl_4^-$ ratios, the reduction became faster, the number of crystal seeds increased, and the spherical shape was favored. The reduction was found more efficient and faster in the presence of Tetronic T904 compared with that in Pluronic P105 (which has a comparable number of EO and PO units with Tetronic T904) [69]. This has been attributed to the more open conformation of the star-shaped Tetronic that facilitates the formation of crown ether-like cavities by the PEO blocks, but also by the presence of reducing amino groups (as discussed below). The authors also concluded that T904 exhibits a better stabilization capacity, presumably because of its star architecture [69]. The presence of the amine group in the polymer molecule conferred sensitivity to the solution pH. In particular, the particle size increased when the synthesis was carried out in acidic conditions. This has been attributed to a decreasing number of nuclei, as the protons inhibit the PEO blocks of the polymer from interacting and reducing the metal ions [69], but could also reflect a change due to pH in the block copolymer conformation and/or structure of the micelles.

Members of a related family of block copolymers, amino-terminated PEO–PPO block copolymers (Surfonamine), were recently reported to reduce $HAuCl_4$ and form gold nanoparticles under some heating, and at sufficiently long PEO blocks [70]. The Surfonamine polymers could bind to the surface of the gold nanoparticles, resulting on an enhanced-activity for gold ion reduction at that location. The strong binding of these block copolymers resulted in nanoparticles with different surface properties, depending on the polymer PEO/PPO ratio. For example, gold nanoparticles synthesized in Surfonamine L-207 ($EO_{33}PO_{10}NH_2$) could mix well with water but not with cyclohexane. On the other hand, gold nanoparticles synthesized in Surfonamine B-200 ($EO_6PO_{29}NH_2$) were miscible in cylcohexane but not in water [70].

In the two studies highlighted above, the presence of amine groups conferred further functionality to the PEO–PPO block copolymers. Alkylamines have been previously investigated as capping agents for the surface modification of gold nanoparticles to render them dispersible in organic solvents [71]. The binding of alkylamines with the gold surface can be due to the formation of an electrostatic complex between protonated amine molecules and surface-bound $AuCl_4^-$/$AuCl_2^-$ ions, and/or a complex of the form [$AuCl(NH_2R)$] [71]. In 2004, the same year when the spontaneous synthesis of gold nanoparticles in aqueous PEO–PPO block copolymer solutions was first reported [40], it was recognized that amines can also function as reductants [72]. Gold nanoparticles were prepared in water by oleyl-amine that can electrostatically complex with $AuCl_4^-$ ions, reduce them, and cap the resulting gold particles to colloidally stabilize them. The reduction could take place at ambient conditions, but was considerably enhanced at 50 °C [72]. We note that, in order for the synthesis methodology to be effective, the ability of amines to reduce gold ions and to bind to metallic gold needs to be combined with a dispersion stabilization function. In what follows we review several studies directed toward this aim.

3.2. Amine-containing block copolymers and dendrimers

A diblock copolymer consisting of α-biotinyl-PEO and poly[2-(N,N-dimethylamino)ethylmethacrylate] (PDMA) could achieve reduction of $HAuCl_4$ in aqueous solution at room temperature, resulting in PEO-modified gold nanoparticles with biotin recognition moieties at the end of the PEO chains [37]. The nanoparticles had a size in the range 6–13 nm, depending on the initial $AuCl_4^-$/polymer ratio, and exhibited high dispersion stability in water. A related diblock copolymer, consisting of the biocompatible poly(2-(methacryloyloxy) ethyl phosphorylcholine) (PMPC) block and PDMA, mediated the aqueous solution synthesis of sterically stabilized gold nanoparticles at ambient temperature without any additional reducing agent [73]. The authors indicate that the PDMA block becomes partially protonated upon addition of $HAuCl_4$, and the remaining nonprotonated tertiary amine groups reduce the gold ion to metallic gold. PDMA is adsorbed on the gold nanoparticle surface while PMPC serves as a stabilizing block. The size and shape of the gold nanoparticles could be controlled by tuning synthesis parameters such as the block ratio and the concentrations of the PMPC–PDMA polymer and $HAuCl_4$ [73].

Assemblies by functional polymers can serve to localize the formed nanoparticles. For example, gold nanoparticles were synthesized within the corona of micelles formed in aqueous solution by the diblock copolymer poly[tert-butylstyrene-b-sodium (sulfamate/carboxylate-isoprene)] (BS-SCI) [74]. The metal precursor, $HAuCl_4$, coordinated with the anionic SCI corona of the micelles, and was subsequently reduced by the amine groups present there. The polyelectrolyte nature of the hybrid BS-SCI/gold micelles resulted in colloidal stability that depended on the solution pH and ionic strength [74]. Gold nanoparticles (of 30–50 nm diameter) were prepared on the surface of liposomes (with diameter of 50–200 nm) formed by distearoyl-N-monomethyoxy PEO-succinyl-phosphatidylethanoamine (DSPE–PEO) and L-alpha-dipalmitoylphosphatidylcholine (DPPC) [75]. The synthesis proceeded in aqueous solutions at ambient conditions in the absence of any reducing agents or energy input [75].

Poly(allylamine) (PAAm) was used as a reducing and stabilizing agent for the single-step synthesis of gold nanoparticles in aqueous solution [76]. The PAAm that was adsorbed on the surface of these nanoparticles could be exchanged with a variety of omega-functionalized acid-, alcohol-, amine-, and biotin-terminated alkylthiols [76]. Gold nanocrystals with different shapes, wire, sheet, octahedral, and decahedral, were synthesized by in situ reduction within gels formed by low molecular weight tryptophan-containing peptide amphiphiles in water, without using any external reducing or capping agents [77]. The authors noted that the gel morphology plays an important role in the preparation of the different nanocrystal shapes [77].

Gold nanoparticles have been synthesized and stabilized within poly(amidoamine) (PAMAM) dendrimers. For example, hydroxyl-functionalized dendrimer-stabilized gold nanoparticles can be formed by simply mixing glycidol hydroxyl-terminated poly(amidoamine) dendrimers

of generation 5 (G5.NGlyOH) with $HAuCl_4$, and acetamide-functionalized dendrimer-stabilized gold nanoparticles can be formed by acetylation of amine-terminated G5 PAMAM dendrimers (G5.NH2) complexed with $AuCl_4^-$ ions [78]. In both cases, no additional reducing agents were required, and the reactions were completed at room temperature. All of these functionalized nanoparticle-dendrimer hybrids are water-soluble and stable [78]. Gold nanoparticles also formed spontaneously by simply mixing generation 4 (G4) or 5 (G5) glycidol-modified PAMAM dendrimers with $HAuCl_4$ in either methanol or water at room temperature [79]. The size of the formed nanoparticles can be varied through a change of the dendrimer generation or solvent. The use of 1,2-epoxyhexane-modified G4 PAMAM dendrimers can allow for tuning of the surface hydrophilicity of the gold nanoparticles [79]. Amine-terminated hyperbranched poly(amidoamine) in aqueous solution served as both reductant and stabilizer for the preparation of silver nanoparticles with size in the range 4–15 nm, adjusted by the initial polymer/Ag ratio [80]. PEGylated Percec-type dendrons in arene-cored dendrimers were found capable of the spontaneous reduction of $HAuCl_4$ and stabilization of dendrimer-stabilized gold nanoparticles in water, in the absence of other reductant [81].

4. Morphogenesis of anisotropic metal nanoparticles in functional polymer solutions

Motivated by the intriguing shape-dependent properties exhibited by nanostructures, significant efforts have been extended in tailoring the shape of materials at the nanoscale [9,10,21,82,83]. For example, the sharp tips and edges found in nanoparticles are regions of high electric field that greatly enhance optical effects [83]. Also, nanoparticles with different faces have different densities of adsorption sites, and thus catalysts of the same material but with different shapes can exhibit very different performance [13]. In what follows, we discuss how PEO-containing block copolymers can direct the synthesis of non-spherical metal particles.

4.1. Nanoplates

In a study of the effects of PEO–PPO–PEO block copolymer concentration and PEO and PPO block lengths on the size of gold nanoparticles synthesized from $HAuCl_4$ in aqueous solutions, Sakai and Alexandridis [84] found that an increase of the $HAuCl_4$ concentration caused a change in the particle shape from spherical to triangular or hexagonal nanoplates (Fig. 2). In a paper published in the same year, Wang et al. [85] reported the synthesis of crystalline gold nano- and microplates with triangular or hexagonal shapes by reduction of $HAuCl_4$ in lyotropic liquid crystals (LLC) [86,87] mainly made of PEO–PPO–PEO block copolymers and water after adding a small amount of cetyltrimethylammonium bromide (CTAB) or tetrabutylammonium bromide (TBAB). The formation of microplates occurred at an optimal value of CTAB or TBAB concentration, and was attributed to the selective adsorption of CTAB or TBAB on certain crystallographic facets of the growing gold crystals [85]. Although the block copolymer LLC structure does not really act as a template, Wang et al. [85] hypothesized that it provided a certain ordering that confined CTAB as well as the metal nuclei, and facilitated the consequent growth of single-crystal plates. To test this hypothesis, Sakai & Alexandridis [88] considered the synthesis of gold microplates through autoreduction of $HAuCl_4$·in aqueous solutions of the PEO–PPO–PEO block copolymer Pluronic L64 at ambient conditions, in the absence of added energy, reductant, or other surfactants. Pluronic L64 forms both cylindrical/hexagonal and lamellar lyotropic liquid crystals, as well as micellar solutions [86]. It turned out that crystalline microplates could form across a wide Pluronic L64 composition range. The plate morphology has been attributed to gold ion reduction on the {1 0 0} facets (promoted by the lower reduction activity of the relatively short PEO length Pluronic L64 block copolymers that adsorb there), rather than the shape-directing action of LLCs as templates [88]. Triangle and hexagonal gold nanoparticles have also been obtained by $HAuCl_4$ reduction in mixed micelles of Pluronic P103 + P84 and P103 + P123, but, interestingly, not in the micelles

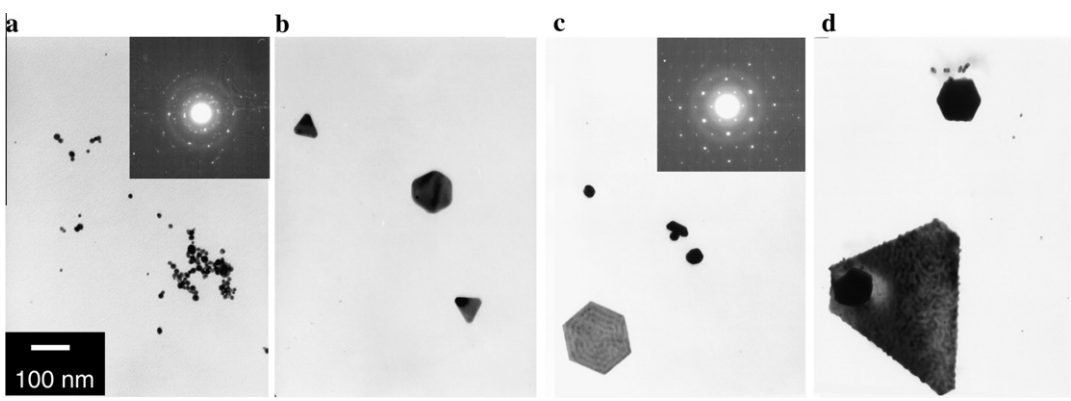

Fig. 2. TEM of gold nanoparticles produced in 5.0 mM Pluronic P105 aqueous solutions at different $HAuCl_4$ concentrations: (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.8 mM L^{-1}. The scale bar represents 100 nm. Note the transition from spherical nanoparticles to triangular or hexahedral nanoplates occurring with an increase in the $HAuCl_4$ concentration [84]. Also note the hexagonal symmetry spots in the electron diffraction pattern shown in the insets.

of the individual Pluronic block copolymers, under the same conditions [89].

Single-crystalline gold nanoplates formed in aqueous solutions of PEO–poly(styrene oxide) block copolymers in the 30–65 °C temperature range [47]. The nanoplates were of mostly truncated or rounded triangular shape, with {1 1 1} planes as the basal surfaces, and lateral mean sizes in the range 0.1–1.2 μm (depending on polymer concentration and reaction temperature). The authors point out that the surface energy of nanoplates is much higher compared to that of cubooctahedra and multiply twinned particles, thus the nanoplate formation would require kinetic control. This was attributed to the hydrophobic functional polymer used, which does not facilitate pseudo-crown ether cavity formation for metal nuclei reduction. The polymer most likely adsorbed selectively on the lowest energy {1 1 1} planes of the nanocrystals, inhibiting their growth. This promoted anisotropic growth along the {1 0 0} orientation [47]. The reaction temperature was shown to be very important for nanoplate formation. At room temperature, the reaction was faster, growth occurred in all crystallographic directions and spherical nanoparticles with sizes in the range 20–70 nm were formed. At higher temperatures (above 70 °C), only polydisperse, irregular particles were produced from a rather slow reduction [47].

Single-crystalline gold nanoplates were produced when sodium chloride was added to an aqueous Pluronic P123 solution at a molar ratio $NaCl:HAuCl_4 = 10:1$ [90]. The chloride ion is thought to act by facilitating the growth of {1 1 1} oriented hexagonal/triangular gold nanoplates. It is well known that Cl^- ions chemisorb on the surface of gold to form a hexagonal closed packed adlayer on the Au (1 1 1) surface, and inhibit the growth along the ⟨1 1 1⟩ direction [91]. Thus, Cl^- ions promote the crystal growth perpendicular to the ⟨1 1 1⟩ direction required for the formation of the flat gold nanoplates. The degree of formation of the gold nanoplates was found proportional to the concentration of Cl^- ions. The authors proposed that the increase of the Cl^- concentration, enhanced the oxidative etching and dissolution of twinned seeds [92,93], so that more single-crystal seeds (free of twin boundary defects on their surface) were produced, and, consequently, more single crystalline nanoplates formed than multiple-twinned icosahedra [90].

Gold nanoplates were also produced when LiCl or KCl were added to the aqueous solution instead of NaCl. However, gold nanocrystals with irregular shapes were produced when NaBr or NaI were added [90]. While the hexagonal packed adlayer of Cl^- is well aligned with the Au (1 1 1) surface, the bromide or iodide ion adlayer has a large mismatch with the Au (1 1 1) surface and generates interfacial strain [94]. This strain prevents the gold crystals from growing with extended (1 1 1) faces. NaBr and NaI thus favor gold particles with irregular shapes [90].

4.2. Icosahedra

The synthesis of icosahedral (30 sharp edges and 12 corners) gold particles using $HAuCl_4$ as a precursor and PEO–PPO–PEO block copolymers as both reductants and directing agents has been reported by Zhang et al. (see Fig. 3) [95]. The particles size could be tuned from 100 nm to 1 mm by varying experimental conditions. For example, the size decreased with increasing concentration of Pluronic F88, presumably because of the higher block copolymer amount on the particle surface that inhibited particle growth. The size also decreased when a more hydrophobic polymer was used, e.g., nanoparticles with sizes of about 100–250 nm formed in the presence of Pluronic P105. More regular icosahedral gold nanoparticles were formed when a high molecular mass block copolymer was used. This was attributed to more efficient absorption of the higher molecular weight mass on the surface of gold clusters. The results suggested that the gold icosahedral particles formed at an early stage in the reaction [95].

Gold icosahedra with an average diameter of about 600 nm have been prepared by heating an aqueous solution of the PEO–PPO–PEO block copolymer Pluronic P123 and $HAuCl_4$ at 60 °C for 25 min [90]. The authors hypothesized that Pluronic P123 selectively adsorbs on Au crystal faces to promote the anisotropic growth toward the formation of gold icosahedra. The authors pointed out that an icosahedron, which is a type of multiple-twinned particle (MTP), tends to achieve a low total free energy by assuming a twinned structure with the lower energy {1 1 1}

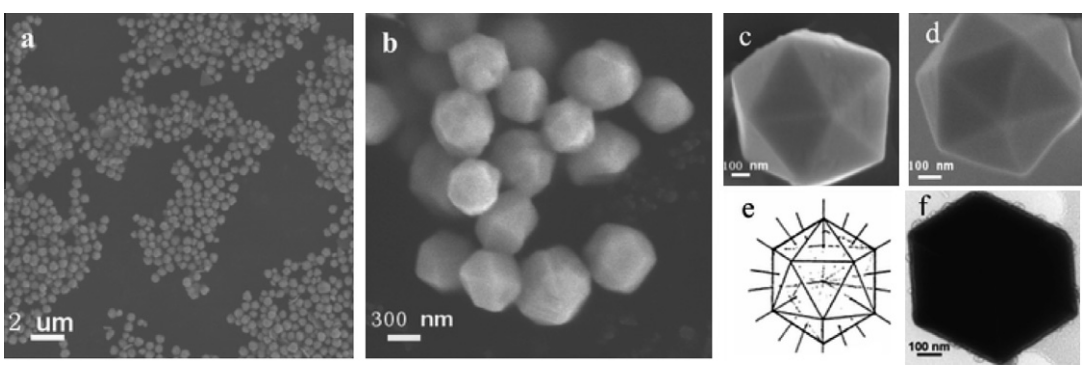

Fig. 3. Gold icosahedra synthesized at 40 °C from 0.84 mM and 5.8 mM Pluronic F88 and $HAuCl_4$, respectively, following reaction for one day [95]: (a) SEM image; (b) higher magnification SEM image; (c) and (d) SEM images of a single gold particle observed from different angles of view; (e) geometrical model of the obtained icosahedral particles; (f) TEM image.

facets. Because of lattice distortions and surface defects, however, this twinned structure exhibits strong reactivity toward oxidative etching [92]. Furthermore, the strain energy emanating from the twin defects increases as the MTP size increases [93]. Thus, it is generally thought that MTPs are not stable when they grow to a large size. The authors stipulated that the surface capping ability of Pluronic P123 reduced the surface energy, so as to offset the strain energy of the twinned structure, and protected the gold icosahedra from oxidative etching [90]. Hence, Pluronic P123 was able to stabilize the growth of large multiple-twinned icosahedra.

4.3. Anisotropic metal nanostructures mediated by poly(vinyl pyrrolidone) polymers

Poly(N-vinyl-2-pyrrolidone) (PVP) is a water-soluble polymer, which, similarly to PEO, can provide multiple functions, as homopolymer or part of a copolymer, in the synthesis of metal nanomaterials. PVP was initially used as a colloidal stabilizer, but it was recognized in 2006 that it could also serve as a reductant of metal salts in aqueous solutions to produce gold and silver colloids in a one-step process, at low temperatures, without the addition of any other reducing agent [96]. Two possible mechanisms were initially proposed for the PVP-mediated reduction of metal ions: direct hydrogen abstraction induced by the metal ion, and/or reducing action of macroradicals formed during degradation of the polymer [96]. More recent mechanistic studies revealed that water plays an important role in this synthesis: as a nucleophile, it attacks the gold-vinyl complex, leading to the production of an alcohol-based Au^{-1} intermediate [97]. This intermediate then undergoes a redox reaction in which Au^{-1} is reduced to Au^0, leading to the formation of Au clusters, together with a carboxylic acid in the final product [97].

Various gold nanostructures, such as decahedral and icosahedral particles, and plates, have been synthesized through heating of a PVP/$HAuCl_4$ aqueous solution, with the ratio of polymer OH end-groups to Au ions identified as an important parameter for varying the particle shape [98]. PVP reduction of $HAuCl_4$ in aqueous solutions in the absence of any additional capping agent or reductant, led to anisotropic gold nanostructures with morphology that evolved from nanotadpoles to nanokites, and then triangular and hexagonal microplates as the $HAuCl_4$ amount increased [99]. The authors noted that the mild reducing power of PVP, resulting in a slow reduction rate, played an important role in the formation of nanoplates during nucleation, and in their growth into highly anisotropic nanostructures [99]. The same group reported a protocol that generated gold icosahedra of about 18 nm in size in high yields by simply mixing aqueous solutions of $HAuCl_4$ and PVP [97]. This protocol was also used to prepare multiply twinned silver nanoparticles (15–20 nm), spherical aggregates (25–30 nm) of Pd nanoparticles, and very small (2 nm) Pt nanoparticles [97]. Triblock copolymers with PVP end-blocks and the biodegradable poly(ε-caprolactone) (PCL) as a middle block have been reported to both reduce $HAuCl_4$ in aqueous solution and stabilize the resulting nanoparticles [100].

4.4. Networks and dendritic nanoparticles

Spherical Au-Ag core–shell nanoparticles and Ag-Au bimetallic nanonetworks (i.e., spherical Au or Ag nanoparticles connected by Ag or Au nanowires, respectively) have been synthesized in the same solution (“one pot”) in the presence of PEO–PPO block copolymers but in the absence of any additional agents and/or energy input [59,101]. The networks of Ag nanowires connecting Au nanoparticles grew with an increase in Ag^+ concentration, and the Ag nanowire length reached up to about 600 nm. The Ag nanowires grew from the surface of Au nanoparticles, but Ag did not appear to cover the Au nanoparticles. In the case of Au-networked Ag nanoparticles, Au was shown to cover the Ag nanoparticles [59].

Dendritic platinum nanoparticles have been synthesized in high yield via a one-step aqueous-phase reaction mediated by Pluronic F127 block copolymer from the reduction of a platinum complex by ascorbic acid without the need for organic solvents, templates, or ion replacements. According to the authors, the as-prepared dendritic platinum nanoparticles have the highest surface area ($56\ m^2\ g^{-1}$) of all reported unsupported platinum materials [102]. To understand the role of the PEO–PPO–PEO block copolymer in this system, investigations were done by replacing Pluronic F127 with different surfactants. It was known that Pluronic was critical for the formation of the dendritic nanoparticles, with a mechanism (i.e., cavity structure in aqueous solution, and adsorption onto the surface of the formed metal) similar to that in the synthesis of gold nanoparticles. The Pluronic F127 concentration used was lower than its cmc [102]. The same group reported the Pluronic F127 facilitated the synthesis of bimetallic colloids consisting of a Au metal core coated with a nanodendritic Pt shell [103].

5. Metal nanoparticle organization in block copolymer matrices

The use of functional polymers, such as block copolymers, brings additional potential benefits that go beyond the (localized) influence of the polymer on the crystallographic habit (discussed above in the context of the synthesis of anisotropic particles), and into longer-range templating or structuring. Templates generated by the self-assembly of block copolymers are particularly attractive because of their reproducible (thermodynamically driven) formation, morphological versatility, characteristic dimensions in the nanoscale, and processability [26–30]. For example, self-assemblies of block copolymers of the poly(ethylene oxide)-poly(propylene oxide) family [48,53,104,105] have been used successfully for templating the synthesis of inorganic [106–108] and semiconductor [109–113] nanomaterials.

Variation of the block copolymer molecular characteristics (e.g., block length, block ratio), the temperature, and/or the addition of selective solvent (of a certain type/quality and concentration), allows for a unique tunability of the block copolymer phase behavior and corresponding nanostructure [6]. The PEO–PPO–PEO block copolymers,

discussed previously in this review, form self-assemblies in the presence of water (selective solvent for PEO) that can transform from spherical micelles to lyotropic liquid crystals (ordered spheres, cylinders, or lamellae) with an increase in the block copolymer concentration (at a fixed temperature) [86,114,115]. Replacement of part of the water with an organic solvent that has more favorable interactions with PPO can result in the evolution of structure from water-continuous to organic solvent-continuous ("water-in-oil" or "reverse") [87,115–119].

Spontak et al. [120] compared the incorporation within block copolymer matrices of low-molar-mass compounds or nanoparticles, using a self-consistent field theoretical approach to quantitatively evaluate their segregation and interfacial excess as functions of block selectivity and inclusion size, and concluded that there is a wide correspondence in the structure-forming effect of molecular and of nanoscale inclusions. This correspondence provides opportunities for the elucidation of the effects of metal nanoparticle incorporation in ordered block copolymers, in a manner analogous to the effects of solvents that preferentially localize in the domains formed by a certain block, or at the interfacial region between different blocks [117].

The best studied ordered block copolymer – metal nanoparticle systems involve gold nanoparticles that have been appropriately functionalized in order to localize within the ordered domains formed by polystyrene-poly(2-vinylpyridine) (PS-P2VP) block copolymers. The location of gold nanoparticles can be controlled through varying the (i) surface coverage of gold nanoparticles by end-attached polymer ligands [121], (ii) molecular mass of the polymer ligands [122], (iii) chemical composition of the polymer ligands [123], or (iv) nanoparticle concentration [124,125]. The bare gold nanoparticles have a more favorable interaction with the P2VP block of the PS–P2VP block copolymers. Modification of the gold surface with thiol terminated polystyrene homopolymers (PS–SH) has been shown to drive the nanoparticles toward the PS domains [121]. The areal density of PS chains on the gold particles has been found important for controlling the nanoparticle location in the block copolymer templates. Nanoparticles with PS chain areal density >1.6 chains/nm^2 were found dispersed in the PS domains of the PS-P2VP block copolymers, whereas for PS chain areal density <1.3 chains/nm^2, the nanoparticles were localized at the interface between the PS and P2VP domains [121]. The chain areal density below which the Au–PS nanoparticles were found to adsorb to the PS–P2VP interface decreased as the PS–SH molecular mass increased [122]. Gold nanoparticles functionalized with both PS–SH and thiol terminated poly(2-vinylpyridine) homopolymers (P2VP–SH) were found to localize at the PS/P2VP interface of the lamellar block copolymer morphology across a wide range of PS and P2VP surface compositions [123]. This was attributed to a redistribution of PS and P2VP polymer chains on the Au surface, effectively rendering the nanoparticles amphiphilic and prone to partitioning at the PS/P2VP interface (see Fig. 4) [123].

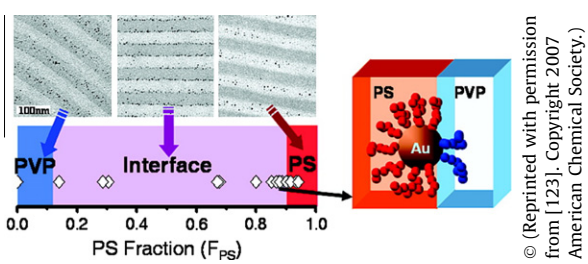

Fig. 4. Gold nanoparticles that have been functionalized by a mixture of PS and P2VP at a high chain areal density coverage, are localized in different domains within lamellar PS-P2VP block copolymer templates, depending on the PS fraction in the PS and P2VP mixture [123].

An investigation of the self-assembly of PS–SH functionalized gold nanoparticles in microphase-separated PS-P2VP block copolymers as a function of particle concentration showed that, at 8.8% Au loading, the Au nanoparticles remain well dispersed in the lamellar polymer matrix, whereas at 27.0% Au loading the polymer morphology transformed to a hexagonal packed cylinder phase due to the increase in the curvature caused by the higher concentration of the dispersed nanoparticles in the PS domain [124]. The presence of nanoparticles amplified the local compositional fluctuations, and created conditions to induce disorder in the polymer morphology. At high particle loading, packing constraints prevented all particles from assembling in the PS domain, and the excess nanoparticles phase separated [125].

6. Opportunities for applications of metal nanoparticle-block copolymer hybrids

Metal nanoparticles coated with functional polymers, either in the context of the "one pot" aqueous solution synthesis and stabilization methodology highlighted previously, or in a separate, physical adsorption or chemical reaction step that follows the nanoparticle synthesis, have been considered for a variety of novel applications. Some applications emanate primarily from the metal nanoparticle character, but they benefit tremendously from the colloidal stability, dispersibility in aqueous media, and biocompatibility conferred by the PEO- or PVP-containing functional polymers. Examples include catalysis in aqueous media [126], antimicrobial activity [80], novel optical properties (such as adsorption in the near-infrared region, NIR, of the electromagnetic spectrum which is of interest to optical filters and coatings) [47,127], and formation of metal nanowire networks, films, or nanocomposites [101,128,129]. Other applications rely mostly on the polymer coating side, e.g., molecular recognition [37], and cellular uptake [62], but they benefit from the solid metal core of the hybrid.

More notably, several applications are based on a unique combination of the metal core and the polymer coating [130–132]. In an example of metal nanoparticle-block copolymer hybrids that hold potential for diagnostic and therapeutic applications, gold nanoparticles were reacted with Pluronic F127 block copolymer that had its terminal

hydroxyl groups functionalized with thiol, to prepare composite nanoparticles that exhibit a reversibly thermo-sensitive swelling/shrinking behavior emanating from the PPO phase behavior in water [48,49]: the nanoparticle hydrodynamic diameter changed from ~160 nm at 15 °C to ~50 nm at 37 °C [130]. In another example, silver and gold nanoparticles coated with PEO–PPO–PEO block copolymers (Pluronics L121, F68, or F127) have been shown suitable to serve as surface-enhanced Raman spectroscopy (SERS) probes for sensitive and selective analysis of organic analytes [131]. The amphiphilic block copolymer coating promotes the adsorption of organic compounds on the hybrid nanoparticle surface, concentrates locally the analyte molecules, and thus amplifies the Raman signal emitted by the metal nanoparticle [131].

In an elegant combination of (i) the imaging contrast and therapeutic capabilities afforded by NIR-active nanoparticles with (ii) the biocompatibility and biodegradability of a polymer stabilizer, metal/polymer biodegradable nanoclusters smaller than 100 nm with strong NIR absorbance for multimodal application were produced by coating sub-5 nm gold nanoparticles with a block copolymer of polylactic acid and PEO [132]. Individual gold nanoparticles that exhibit NIR absorbance are typically larger than 50 nm, well above the 5 nm threshold size required for efficient renal clearance. The metal/polymer nanoclusters can achieve strong NIR absorbance because of their high content in sub-5 nm gold nanoparticles, while they can clear the body following degradation of the polymer stabilizer over time under physiological conditions, and release of the individual sub-5 nm gold nanoparticles (Fig. 5) [132].

7. Closing remarks

The ability of functional block copolymers to serve as reductants for the synthesis of metal nanoparticles, and, moreover, to control the nanoparticle morphology, confer colloidal stability, and enable long-range ordering is discussed here. These multiple functionalities emanate from the polymer intramolecular conformation (that affords ion-binding and reduction cites) and the supramolecular organization (adsorption on the surface of nanoparticles, formation of micelles), and are exemplified by block copolymers that consist of the water-soluble poly(ethylene oxide) (PEO) and a hydrophobic block such as poly(propylene oxide) (PPO).

PEO–PPO block copolymers can act as reductants and stabilizers in the single-step synthesis and stabilization of metal nanoparticles in air-saturated aqueous solutions, at ambient temperature, in the absence of any additional reductants or energy input. The polymer chemical composition, architecture, molecular mass, and concentration allows for fine- tuning of the size and shape of the resulting nanoparticles. The metal nanoparticles emerge coated with physically-adsorbed polymer that can be subsequently removed or exchanged with other functional ligands, and the nanoparticles can be readily integrated into diverse products (from composites to cells). These attractive features are compounded by the commercial availability of PEO–PPO block copolymers and their biocompatibility, to result in a methodology with favorable cost and low impact to the environment.

A range of other types of functional polymers, solvents, and conditions has been considered in the literature, thus

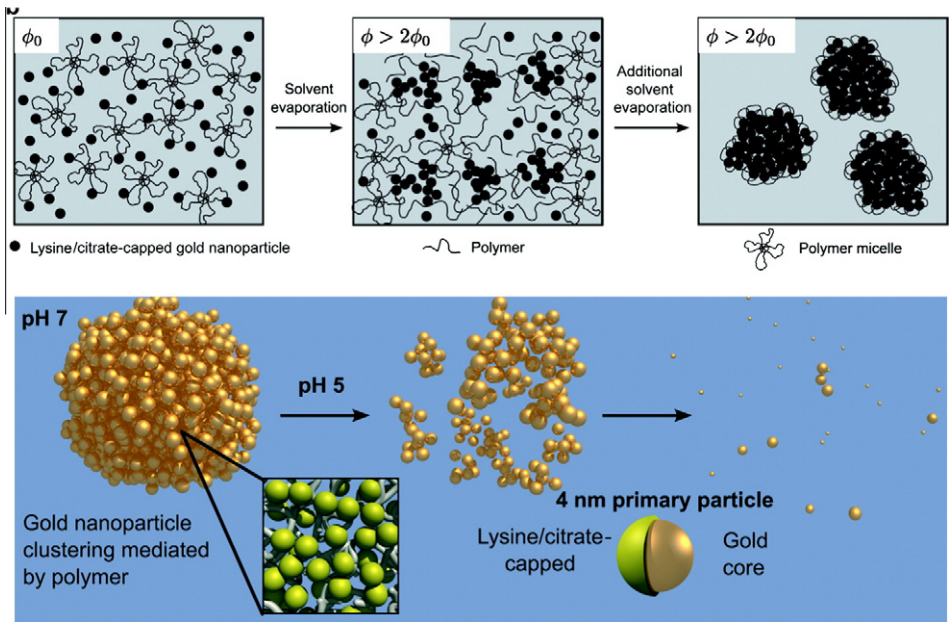

Fig. 5. Schematic of formation and degradation of gold nanoclusters [132]. (top) Primary gold nanoparticles aggregate in the presence of polymer to yield sub-100 nm clusters. The formation of clusters is promoted by polymer adsorption on the nanoparticle surface and solvent evaporation that increases the volume fraction of particles, Φ. (bottom) Sub-100 nm cluster, composed of primary gold nanoparticles that are held together with a biodegradable polymer, deaggregates into primary gold nanoparticles upon degradation of the polymer.

expanding the scope of this methodology. In fact, recent advances in macromolecular synthesis, coupled with an improved understanding of how metal nanoparticles form and grow, provide ample opportunities for the design and development of novel nanomaterials that can be integrated into various devices and processes [133–135]. At the same time, it is gratifying to discover new functions for common, commercially available polymers such as poly(ethylene oxide) and poly(vinyl pyrrolidone).

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